Modeling of the behavior of U, Eu, Pu, Am when heating of radioactive graphite in the carbon dioxide atmosphere

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Abstract. Reactors with gas heat transfer agent have the greatest energy conversion efficiency. They are considered to be the safest. Graphite as part of them is used as moderator and neutron reflector and carbon dioxide can be used as heat transfer. There is a possibility of graphite burning in a carbon dioxide atmosphere at high temperature while the out-project accident. In this project we study the behavior of U, Eu, Pu, Am while heating the radioactive graphite in a carbon dioxide atmosphere by thermodynamic modeling. By thermodynamic modeling the partition of uranium, europium, plutonium and americium at equilibrium phases were obtained.

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In this project we study the behavior of U, Eu, Pu, Am while heating the radioactive graphite in a carbon dioxide atmosphere by thermodynamic modeling.

Full-scale experiments do not always give reliable information at high temperatures due to their complexity and measurements errors. So, calculations were made by thermodynamic modeling using TERRA software which is used for studying systems with complex chemical composition in high temperature conditions.

The software is used to calculate phase composition, thermodynamic and transport properties of arbitrary systems.

The calculation of phase composition and characteristics of equilibrium was made according to reference database for properties of individual substances. The basis of information in the database are thermodynamic, thermophysical and thermochemical properties of individual substances systemized in the Institute of High Temperatures of the Russian Academy of Sciences (database INVATERMO), by national US Bureau of Standards, calculated in Moscow State Technical University using molecular calorimetric and spectrochemical data, published in reference books.

Thermodynamic modeling is successfully used in materials science, physics and fire and explosion safety [2-9].

By thermodynamic modeling the partition of uranium, europium, plutonium and americium at equilibrium phases were obtained.

The uranium phase distribution is shown in Fig. 1. In the temperature range of 373-2273K uranium is in form of condensed U_3O_5. While increasing of the temperature to 2273-3273K there will be decreasing of condensed U_3O_5, increasing of vaporous UO_3 (~ 60%) and increasing of ionized UO_3- (~ 30%), UO_2 + (~ 6%).

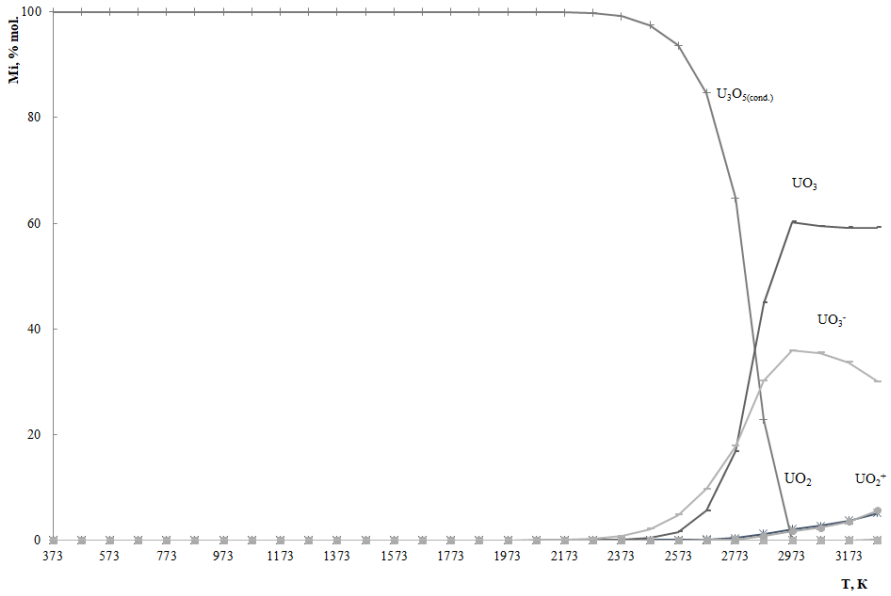

Figure 1. Distribution of uranium by phases

The europium phase distribution is shown in Fig. 2. There is decreasing of condensed $EuCl_2$, increasing of condensed EuOCl and condensed Eu_2O_3 in the temperature range from 373 to 1173K. Ranging from 1173 K to 1573 K a condensed $EuCl_2$ decreases, a condensed Eu_2O_3 increases and a condensed EuOCl decreases and appears condensed EuO. A further increase in temperature to 2173 K leads to decreasing of condensed Eu_2O_3, appearing and increasing of vaporous EuO. When the temperature increases to 3373 K europium is in form of vapor EuO (~ 80%), in the form of ionized Eu + (~ 15%) and in the form of vapor Eu (~ 5%).

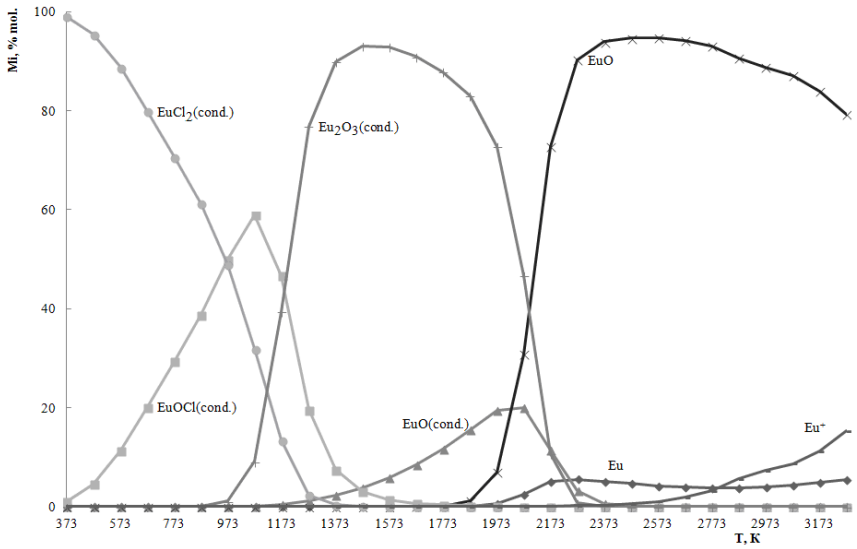

Figure 2. Distribution of europium by phases

The plutonium phase distribution is shown in Fig. 3. At the temperature up to 1873 K almost all plutonium is in the form of condensed PuO_2. By increasing the temperature to 2673 K a condensed PuO_2 disappears and appears the vaporous PuO_2. With the further increasing of temperature a vaporous PuO_2 decreases to 94%, PuO increases up to 3,6 % and an atomic PuO^+ increases up to 2,3 %.

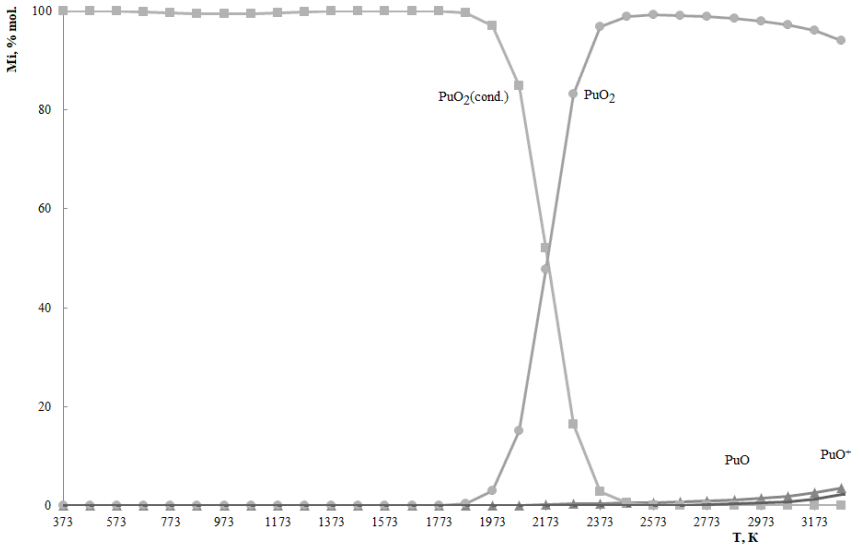

Figure 3. Distribution of plutonium by phases

The americium phase distribution is shown in Fig. 4. At a temperature up to 873 K all the americium is in form of condensed AmO_2. A further increasing in temperature up to 2673 K leads to reducing of condensed AmO_2 (~ 18%), increasing of condensed Am_2O_3 (~ 78%) and appearing of Am vapors (~ 6%). By increasing in temperature up to 3073 K Am vapors increase to 100%, decreases a condensed Am_2O_3 and condensed AmO_2. In the temperature range from 3073 K to 3373 K americium is in the form of vaporous Am.

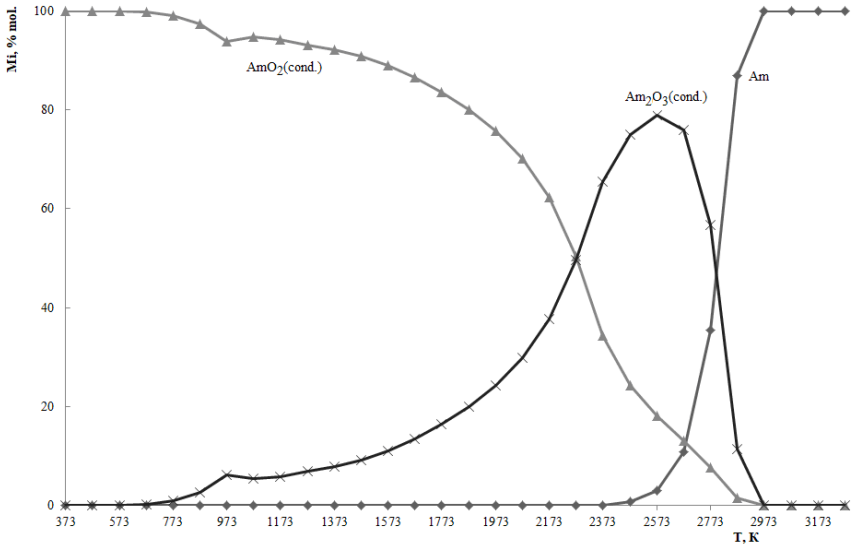

Figure 4. Distribution of americium by phases

The minimum set of basic reactions was written based on the obtained temperature dependences of the radionuclide distribution by phases and numerical simulation results.

$$U_3O_{5(cond.)} + 4CO_2 = 3UO_3 + 4CO \quad (1)$$

$$U_3O_{5(cond.)} + 4CO_2 = 3UO_3^- + 3CO^+ + CO \quad (2)$$

$$PuO_{2(cond.)} = PuO_2 \quad (3)$$

$$PuO_2 = PuO + O \quad (4)$$

$$PuO - e^- = PuO^+ \quad (5)$$

$$2AmO_{2(cond.)} + CO = Am_2O_{3(cond.)} + CO_2 \quad (6)$$

$$Am_2O_{3(cond.)} = 2Am + 3O \quad (7)$$

$$AmO_{2(cond.)} = Am + O_2 \quad (8)$$

$$EuCl_{2(cond.)} + CO_2 = EuOCl_{(cond.)} + ClCO \quad (9)$$

$$EuOCl_{(cond.)} + CO = EuO_{(cond.)} + ClCO \quad (10)$$

$$Eu_2O_{3(cond.)} = 2EuO + O \quad (11)$$

$$EuO_{(cond.)} + CO = Eu + CO_2 \quad (12)$$

$$Eu - e^- = Eu^+ \quad (13)$$

The equilibrium constants of reactions (see Table 2) were determined using concentrations (in mole fractions) of the condensed and gas phase components found in model calculations. Constants are presented in an analytical form:

$$Lnk_i = A + \frac{B}{T} \quad (14)$$

The coefficients A and B for the equation have been calculated by least square method and are consolidated in Table 1.

Table 1. Coefficients of equilibrium constants

Reaction	Temperature range ΔT_i, K	A	B	The value of the approximation R^2
(1)	2073-2973	80,887	-286743,441	1
(2)	2073-2973	57,663	-572327,017	1
(3)	1773-2473	36,169	-77919,521	1
(4)	2673-3273	16,167	-72351,592	1
(5)	2373-3273	9,659	6249,95	0,9941
(6)	1873-2573	15,899	-19978,125	0,9879
(7)	2573-2873	74,974	-352085,43	1
(8)	2373-2973	40,142	-160956,748	1
(9)	673-1073	0,592	-35127,719	1
(10)	1173-1773	5,549	-48077,823	1
(11)	1773-2273	52,285	-205775,396	1
(12)	2073-2273	11,021	-54214,274	0,9999
(13)	2373-2873	19,454	-14997,528	0,9967

The paper presents the computer modeling results for thermal processes with the involvement of U, Eu, Pu and Am during the radioactive graphite heating in the carbon dioxide atmosphere. Temperature dependence diagrams have been obtained as the result of the modeling for the radionuclide distribution by phases in the considered system. Typical reactions and temperature intervals, in which they are observed, have been identified. Temperature intervals of the radionuclide transition from the solid oxide-salt solution to a gas phase have been found. Equilibrium constants have been calculated.

Increasing of the temperature leads to increasing of the constant of balance for all reactions except the reaction (5).

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